



## SYNTHESIS AND CHARACTERIZATION OF SOLID HETEROGENEOUS CATALYST FOR THE PRODUCTION OF BIODIESEL FROM HIGH FFA WASTE COOKING OIL

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### ABSTRACT

*Biodiesel is currently recognized as one of the most promising biofuel alternatives to conventional fossil fuel, considering its number of advantages particularly environmental benign and availability of feedstocks. In this work, newly developed W-Zr /CaO catalyst was synthesized and applied for biodiesel production from high FFA waste cooking oil in a single step reaction process. The newly synthesized catalyst was further characterised by various techniques. Biodiesel yield of 94.1% was achieved under the reaction conditions of 15:1 methanol to oil molar ratio, 2wt% catalyst loading, 80°C reaction temperature and 1h reaction time. The catalyst maintained 79.3% biodiesel yield after five successive reused without regeneration of the catalyst active sites.*

**Keywords:** Biodiesel, Transesterification, High FFA waste cooking oil, Heterogeneous catalyst, Single step reaction process.

### INTRODUCTION

Biodiesel production has recently received the greater attention as reliable alternative biofuel to replace conventional fossil fuel (Atadashi et al. 2012). Petroleum based fuel, though the most popular fuel for internal combustion engines. However, such fuel is associated with possible future depletion of reserves worldwide, global warming as a result of toxic exhaust and non biodegradability (Lee et al. 2014). In the past few years, waste cooking oil (WCO) received excellent recommendations as alternative option low cost feedstock for biodiesel production to expensive feedstock such as palm oil, soybean oil and sun flower oil etc (Ni & Meunier 2007). Transesterification reaction of triglycerides (the major component of vegetable oil) with short chain alcohol (methanol) in the presence of catalyst will produce fatty acid methyl ester (FAME) or biodiesel and glycerol as the by-product (Avhad & Marchetti 2016).

In this study, tungsten-molybdenum and Calcium mixed oxide catalyst was synthesized and characterized for physico-chemical properties using various characterization techniques such X-ray diffraction (XRD), Temperature programmed desorption of carbon dioxide (TPD-CO<sub>2</sub>), Brunei Emmett Teller (BET) total surface area analysis. The catalyst was tested positive for biodiesel synthesis from waste cooking oil.

### MATERIALS AND METHODS

#### Materials

Waste cooking oil (WCO) was obtained from the cafeteria in the Universiti Putra Malaysia. All solvents and reagents used were analytical or high performance liquid chromatography (HPLC) grade. H<sub>3</sub>PO<sub>4</sub>.12WO<sub>3</sub>.xH<sub>2</sub>O (Sigma Aldrich), ZrO<sub>4</sub>H<sub>4</sub> (Sigma Aldrich) and commercial anhydrous Methanol (Merck 99.7%) were purchased from Fisher Scientific company.

#### Catalyst preparation

The catalyst was prepared by incipient wet impregnation method and followed by calcination in a furnace at a temperature of 650°C for 5h. For a typical catalyst preparation, appropriate amounts of ZrO<sub>4</sub>H<sub>4</sub> (sigma Aldrich) and H<sub>3</sub>PO<sub>4</sub>.12WO<sub>3</sub>.XH<sub>2</sub>O was impregnated at 80 °C for 1hr under vigorous stirring after which the resultant solution was mixed with the appropriate amount of powdered CaO and stirred for 3 hrs and followed by drying in an oven at 120°C for 12hrs. and 9wt% denoted as 1W-Zr/CaO, 3W-Zr/CaO, 5W-Zr/CaO, 7W-Zr/CaO and 9W-Zr/CaO, respectively (Ulgen & Hoelderich 2009).

#### Catalyst Characterization

##### Structure and crystalline nature of the catalyst

The structure and crystallite size of the mixed oxide bifunctional catalyst was determined by the powder X-ray diffraction (XRD) technique.

The analysis was carried out on a Shimadzu model XRD6000 power X-ray diffractometer, using Cu, K $\alpha$  radiation (27.7 kW and 30mA) with wavelength ( $\lambda$ ) of 1.54 Å, over the  $2\theta$  range of  $10^\circ$  to  $80^\circ$  with a step of  $0.04^\circ$  at screening speed of 2min/degree. The crystallite size of the catalyst powder was computed using Debye-Scherrer's equation (Wong et al. 2015).

#### **BET Surface area analysis**

Brunauer-Emmet-Teller (BET) surface area, pore volume and pore size distribution of the synthesized catalysts were measured from the multi-point nitrogen adsorption-desorption isotherms (at  $-196^\circ\text{C}$ ) using a micrometrics ASAP 2020 3Flex version 1.02 (Siow et al. 2015).

#### **Basic properties of the catalyst**

The experiments were performed using a Thermo Finnigan TPD/R/O 1100 series apparatus equipped with thermal conductivity detector (TCD). The sample was pre-treated at  $250^\circ\text{C}$  for 30 minutes under nitrogen flow. The sample was pre-treated by heating to  $800^\circ\text{C}$  under the flow of helium at a rate of 30ml/min with heating rate of  $10^\circ\text{C}/\text{min}$  to remove the adsorbed carbon dioxide from the catalyst surface and then cooling down to a temperature of about  $50^\circ\text{C}$ . (Rabiah Nizah et al. 2014).

#### **Experimental design**

The biodiesel reaction was carried out in a 250 ml round bottom flask equipped with a water cooled reflux condenser. 10 g of waste cooking oil sample was introduced into the round bottom flask together with desired amount of methanol and catalyst in each experiment. The reaction took place over a period of 1hr at  $80^\circ\text{C}$  in a close reflux condenser system. After the reaction, the reaction mixture was allowed to cool down and then followed by the separation of the catalyst from the mixture using centrifugation technique. The residual methanol was removed from the product by heating and stirring at  $70^\circ\text{C}$  for 30 minutes on a hot plate. The obtained biodiesel was analysed using GC-FID.

#### **Reusability of the catalyst**

The reusability of the catalyst was performed under the optimized reaction conditions of 2wt% catalyst loading,  $80^\circ\text{C}$  reaction temperature, 15:1 methanol to oil ratio and 1hr reaction time. After completion of each run,

the used catalyst was separated from the reaction mixture and reused without further regeneration treatment.

## **RESULTS AND DISCUSSION**

### **Structure and crystalline nature of the catalyst**

The XRD patterns of W-Zr/CaO bimetallic oxides catalysts with different W-Zr loadings on CaO support are presented in Fig 1. CaO support appeared as intensified peaks at  $2\theta$  of 32.1, 37.2, 53.9, 64.0 and  $67.2^\circ$  (JCPDS File No. 01-082-1691). These peaks reaffirm the presence of cubic CaO. The tetragonal  $\text{WO}_3$  peak was found at  $2\theta$  of  $28.9^\circ$  (JCPDS File No. 00-001-0806). The hexagonal  $\text{ZrO}_2$  peak appeared at  $2\theta$   $22.4^\circ$  (JCPDS File No. 01-089-4770). The patterns also indicate the presence of new metal crystalline phases at  $2\theta$  of 18.6, 48.1 and  $2\theta$  for 58.6 for  $\text{WCaO}$  and  $\text{WZrO}$  respectively. Increase in W-Zr loading on CaO from 3wt% to 9wt% reduced the intensity of the CaO peaks and increasing  $\text{WZrO}$  peaks appear more clearly. High  $\text{W}^{+3}$  and  $\text{Zr}^{+2}$  content reduced the intensity of CaO suggesting the saturation of  $\text{WZrO}$  dispersion which covers the CaO phase of the catalyst and reducing its peak intensity (Ramu et al. 2004). The crystallite size of the catalyst samples decreased linearly with the increase in W-Zr loading on the surface of CaO support as presented in Table 1.

### **BET Surface area analysis**

The specific surface area and pore size of the synthesized catalysts were measured by Brunauer-Emmet-Teller (BET) as presented in Table 1. The results evidently proved that the specific surface area of W-Zr/CaO catalyst decreases with increase in W-Zr loading. The decrease in surface area trend continues from 1W-Zr to 7W-Zr/CaO recording the minimum surface area of  $9.7012\text{m}^2/\text{g}$ . This is due to the low increase in W-Zr loadings on CaO and the trend continue up to a 7W-Zr/CaO loading recording the lowest surface area. This might be as a result of low W-Zr to CaO loadings, which allow the incorporation of W-Zr into the CaO forming homogeneous solid solutions that caused the reduction in specific surface area of the catalysts. However, the surface area increased to  $11.7742\text{m}^2/\text{g}$  when the W-Zr loading increased from 7W-Zr/CaO to 11W-Zr/CaO.

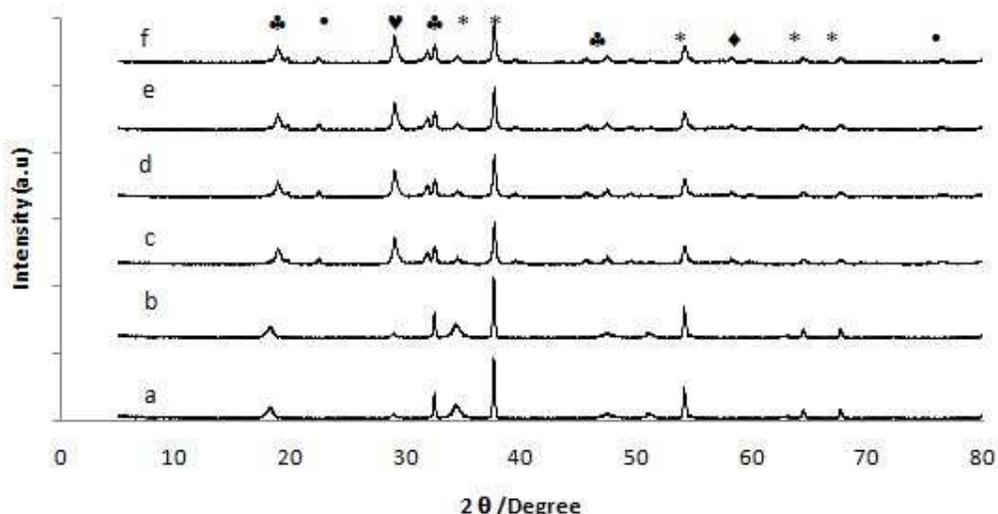


Fig. 1. XRD Patterns of a=CaO, b=1wt W-Zr/CaO, c=3wt W-Zr/CaO, d=5wt W-Zr/CaO, e=7wt W-Zr/CaO, f=9wt W-Zr/CaO calcined at 650°C (5°C/min) for 5h. \*CaO ♣WCaO •ZrO<sub>3</sub> ♥WO<sub>3</sub> ♦WZrO

Table 1. BET surface area, pore volume and pore size and crystallite size of W-Zr/CaO catalyst samples.

Sample	BET Surface area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore size (Å)	Crystallite size (nm)
1W-Zr/CaO	13.8	0.20	568.3	47.4774
3W-Zr/CaO	13.6	0.21	624.2	42.8984
5W-Zr/CaO	10.1	0.18	719.2	29.8417
7W-Zr/CaO	9.7	0.16	648.2	23.2125
9W-Zr/CaO	11.8	0.16	532.3	21.7576

**Temperature programmed desorption of carbon dioxide and ammonia**

Basic strength of these catalysts was determined by TPD-CO<sub>2</sub> as presented in Fig 2. 1W-Zr/CaO, 3W-Zr, 5W-Zr/CaO and 7W-Zr/CaO catalysts samples demonstrates maximum CO<sub>2</sub> desorption peaks at 681, 679, 677, and 675°C, respectively, showing similar desorption peaks trend between the temperature of 675°C to

681°C. This is due to the low loading of W-Zr on to the CaO. When the loading of W-Zr increased from 7 to 9 the catalyst sample desorbed the maximum CO<sub>2</sub> at 618°C as the profiles presented in Fig 2. All the catalyst samples correspond to moderate basic site strength. Hence, increase in W-Zr loading on CaO decreases the basic strength.

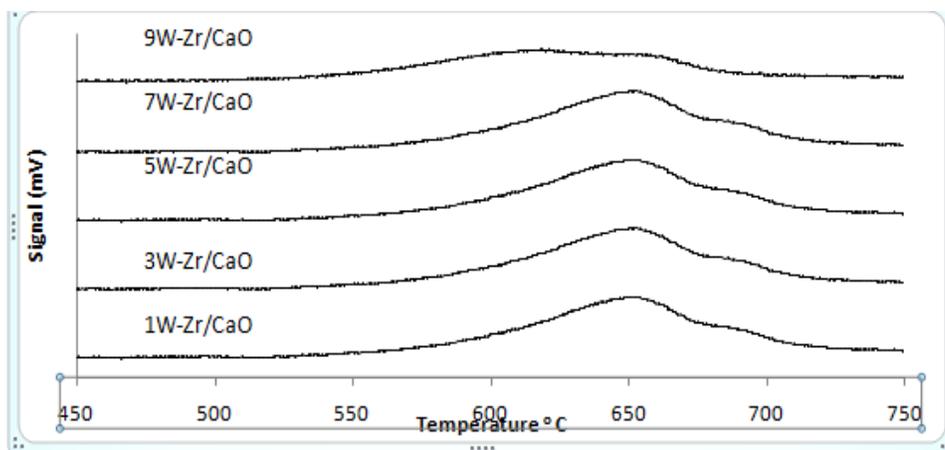


Fig. 2. TPD-CO<sub>2</sub> of W-Zr/CaO mixed oxide catalysts

**Catalytic activity**

The catalytic activity of various fractions of W-bimetallic W-Zr/CaO catalysts on the transesterification of waste cooking oil was determined under the reaction conditions of 2wt % catalyst loading, 80°C reaction temperature, 15:1 methanol to oil molar ratio in 1hr reaction time. The 7W-Zr/CaO catalyst

was qualified to be the best catalyst with the highest catalytic activity of 94% FAME yield. High catalytic performance of the catalyst is attributed to its basicity, and surface area (Wong et al. 2015). The catalytic activity of 7W-Zr/CaO can be related to its moderate basicity. The correlation between FAME yield and desorbed CO<sub>2</sub> is presented in Fig 3.

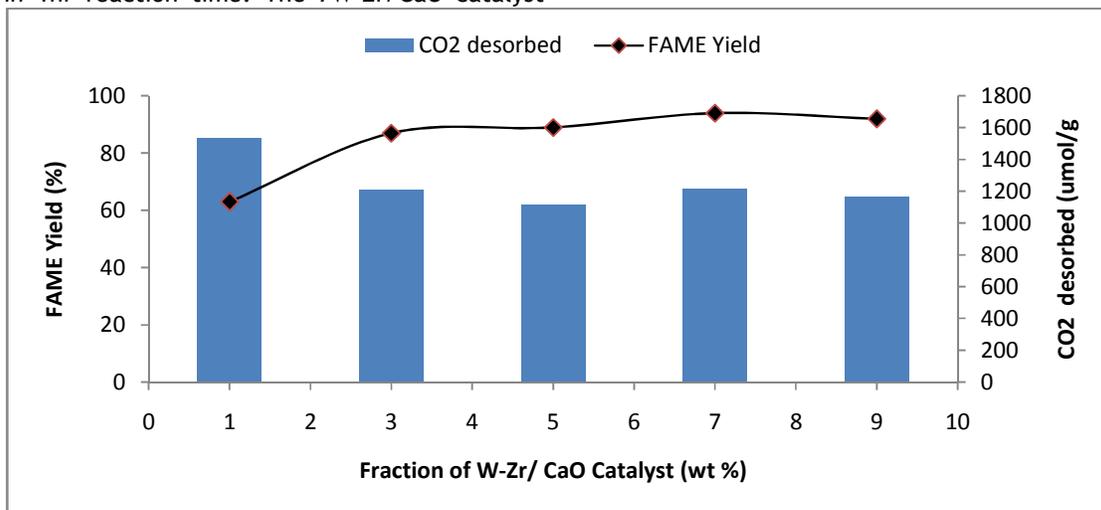


Fig 3. Correlation between basicity and the FAME yield of various compositions of W-Zr/CaO catalyst.

**Reusability test**

The catalyst was successfully reused up to five times before complete loss of activity as presented in Fig 4. Meanwhile, at the end of each reaction cycle, the catalyst was removed and washed thoroughly with hexane and then methanol to clean the catalyst surface from the

polar and non polar components (Kaur & Ali 2015). The drop in biodiesel yield in the fifth cycle was due to deactivation of 7W-Zr/CaO catalyst sample, which might be as a result of adsorption of fatty acid, glycerol or water molecule on the active sites of the catalyst.

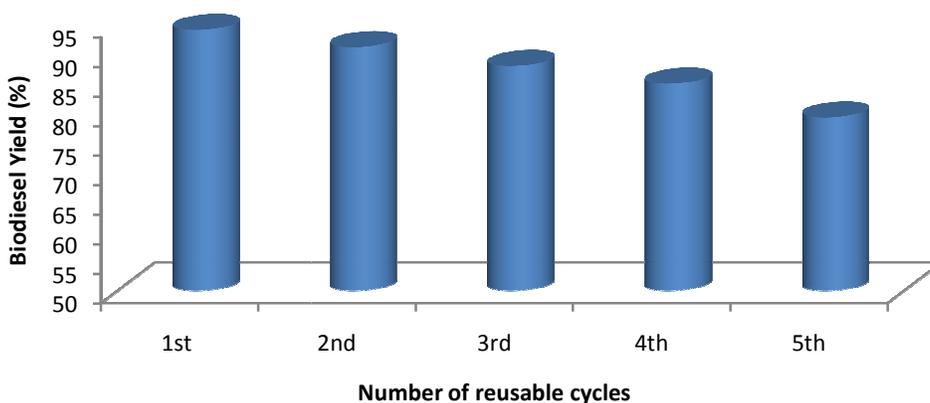


Fig. 4. Reusability of 7W-Zr/CaO catalyst at 1hr reaction time, 80°C reaction temperature, 2wt% catalyst loading and 15:1 methanol to oil ratio.

## CONCLUSION

In this study, W-Zr supported CaO catalysts were synthesized using wet impregnation methods and characterized by various characterization techniques. The catalyst was also tested for transesterification of waste cooking oil to produce biodiesel. 7W-Zr/CaO catalyst sample recorded high biodiesel yield of 94.1% under the reaction conditions of 15:1 methanol to oil molar ratio, 2wt % catalyst loading, 80°C reaction temperature and 1 h

reaction time. Reusability is one of the major advantages of heterogeneous catalysts over a conventional catalyst. 7W-Zr/CaO catalyst maintained 79.3% biodiesel yield after five successive reused without further regeneration of the catalyst activity.

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